Characterization of Nanocomposite Materials for Nuclear Energy Systems Using Synchrotron Radiation

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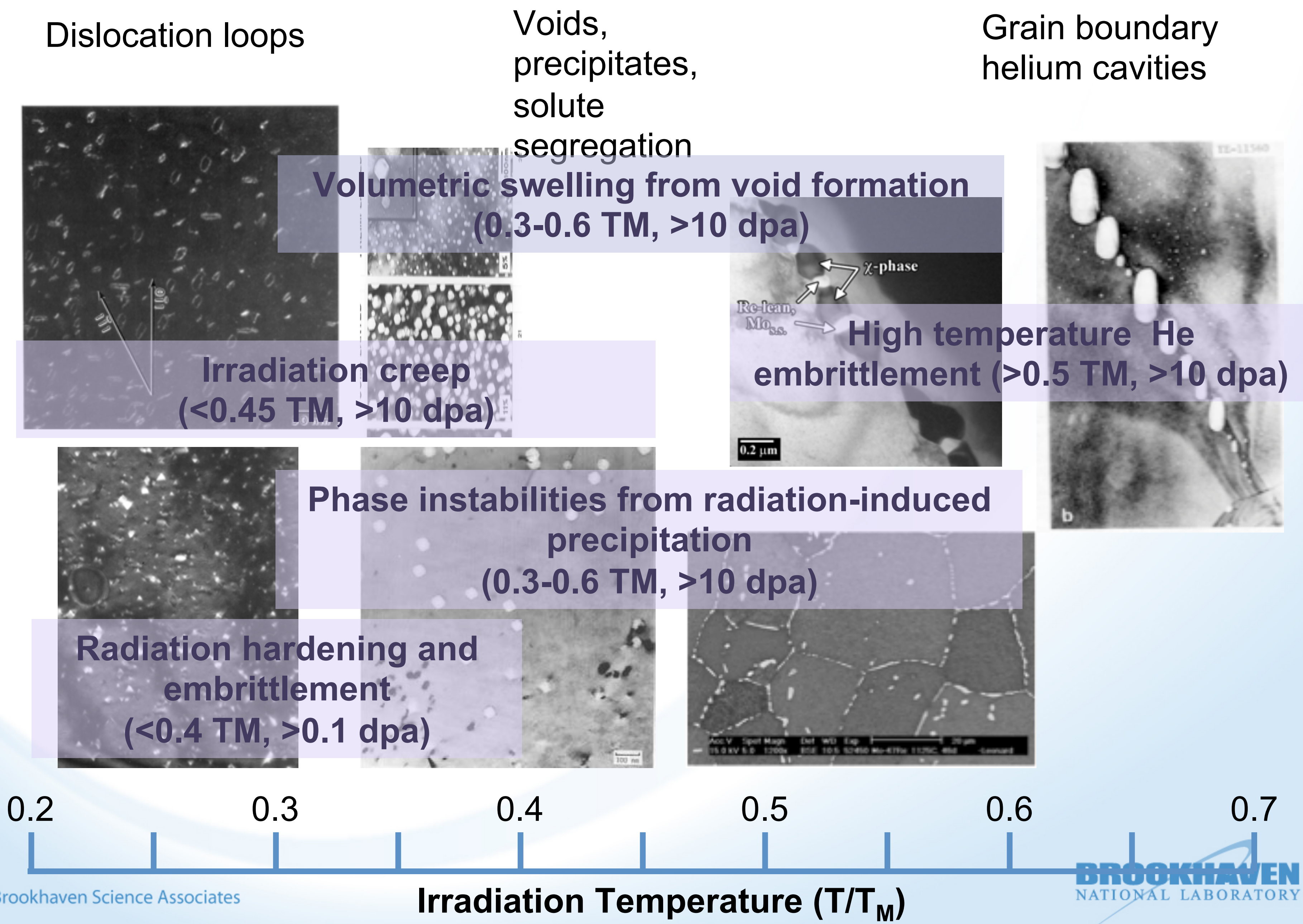
Radiation Damage in Nuclear Energy Systems



Oxide Dispersion Strengthened Steels

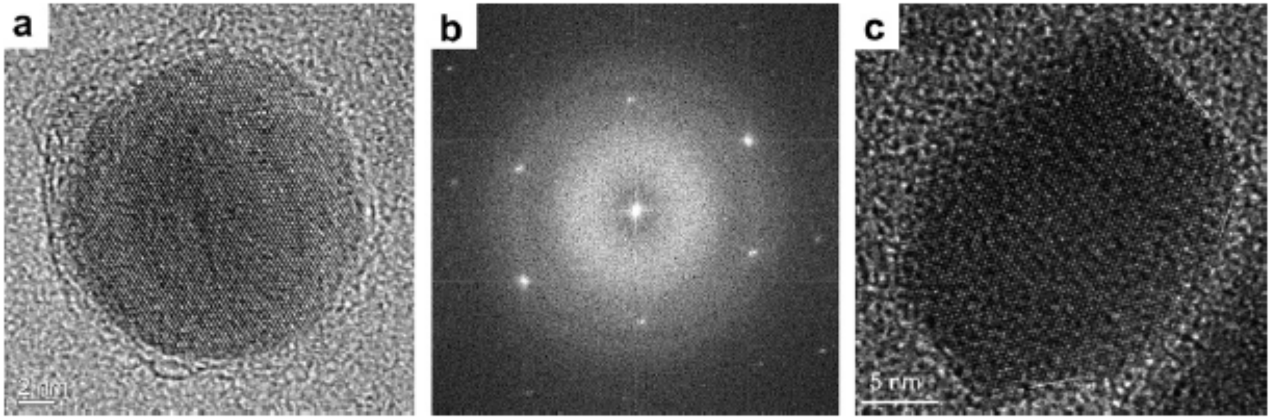


Fig. 8. A HRTEM lattice image of a large feature in (a) US MA957, (b) the corresponding FFT power spectrum and (c) HRTEM lattice image of a large unidentified precipitates (c).

Y. Wu, EM Haney, NJ Cunningham, GR Odette
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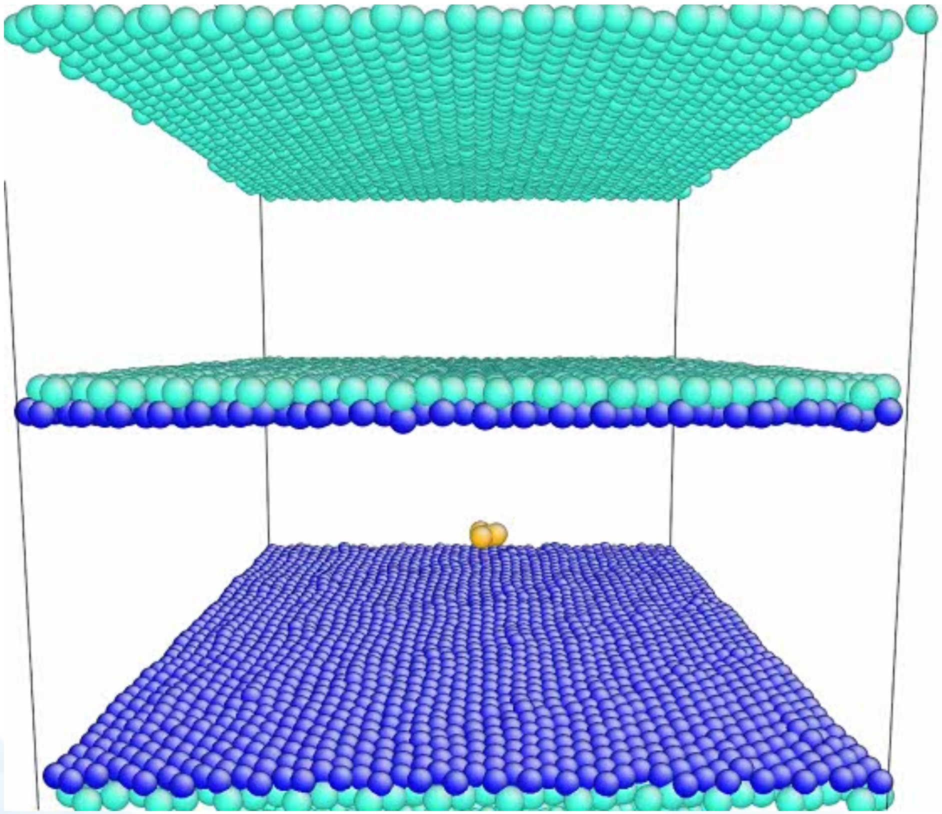
- New reactors require higher temperature materials (550^{o}C), higher dose materials (>200 dpa)
- Oxide Dispersion Strengthened (ODS) Steels are excellent candidates
- Interfaces in ODS Steels are sites for defect recombination, but are geometrically complex and difficult to study
- Six known Y-Ti-O phases
- Atom Probe Tomography suggests highly non-stoichiometric, coherent transition phases
- Some HRTEM-FFT suggests Y_2TiO_5; latest HRTEM suggests small features (d<5nm) to be $Y_2Ti_2O_7$
- DFT models suggests $Y_2Ti_2O_7$ more stable than a coherent transition phase

Model Material System: Cu-Nb Nanocomposite

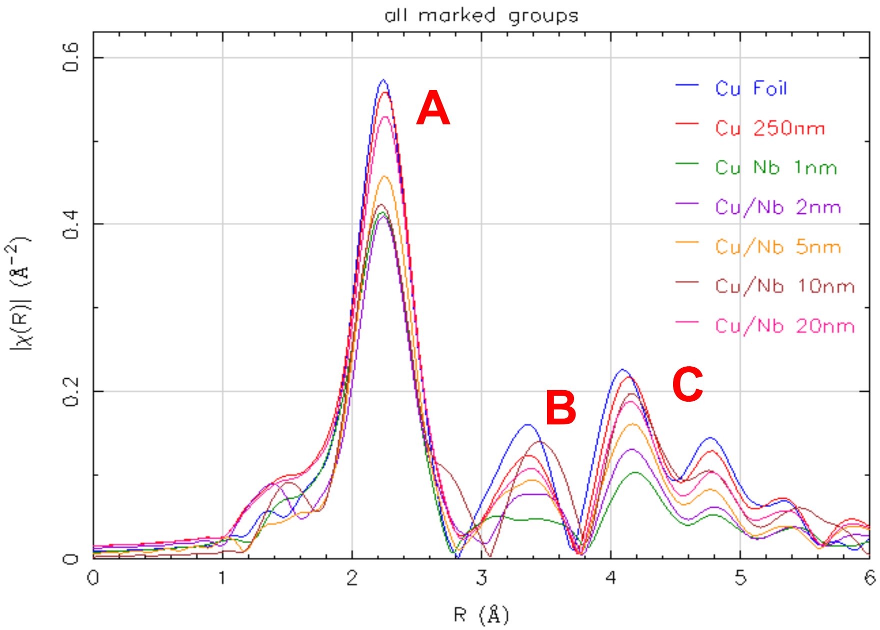
Improved Radiation Tolerance in Nanocomposites

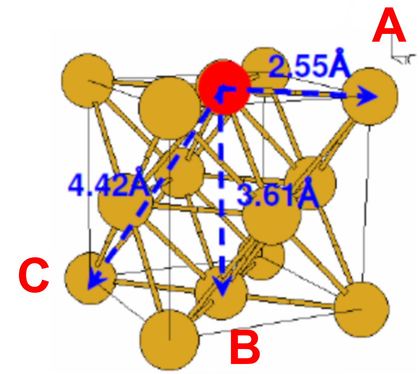
Mike Demkowicz, et al., MIT



- Damage can heal in the vicinity of a Cu-Nb interface
- Measure the defect densities as a function of time
- Study the dynamics of process
- Experiment will validate existing simulations
- New reactors require materials for higher dose

Preliminary Results for Cu/Nb Multilayer Composites





Sample	Cu layer thickness	Relative Percent peak (%)	Missing ordered Cu (%)
Cu Control (250nm)	250nm	99.4	0.6
Cu /Nb (20nm)	20nm	93.3	6.7
Cu /Nb (5nm)	10nm	79.4	20.6
Cu /Nb (2nm)	5nm	71.6	28.4
Cu /Nb (1nm)	2nm	71.3	28.7

Fourier Transform of Copper/Nb nanolayered χ(k) function vs radial distance R(Å). The plots correspond to copper foil as a standard, Cu control sample (250nm) and Cu/Nb nanolayered samples with layer thickness (20nm, 10nm, 5nm, 2nm, 1nm). The total thickness for all samples was kept constant at 250nm.

Modeling EXAFS

- Guess atomic configuration and scattering paths
- Fit the model to the data and analyze parameters from the fit
- When fit is sufficient, accept atomic positions as accurate

MD-EXAFS approach

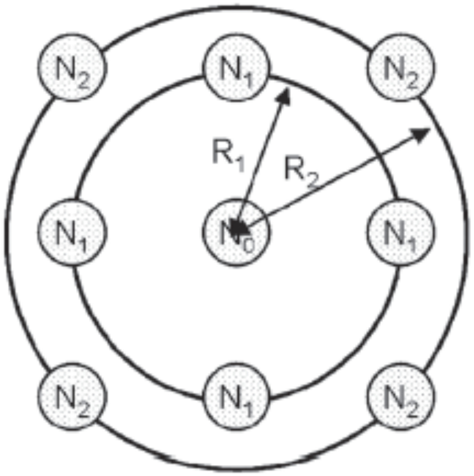
- Molecular Dynamics (MD) simulations can compute atomic positions and path lengths, which can be used to inform an EXAFS analysis.

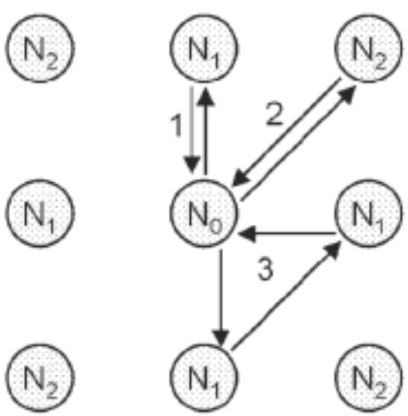
Advantages:

- Large sample accounts for non-gaussian distribution.
- Under-coordination can be incorporated into the fit
- Both sources of disorder – thermal and structural addressed
- Direct comparison of EXAFS measurements with MD simulation, can lead to useful feedback loop between both techniques.

Modeling EXAFS

EXAFS is represented as a sum over all photoelectron scattering geometries:





$$\chi(k,\Gamma) = \mathrm{Im}\left(\frac{(N_\Gamma S_0^2) F_\Gamma(k)}{k R_\Gamma^2} e^{i(2kR_\Gamma + \Phi_\Gamma(k))} e^{-2\sigma_\Gamma{}^2 k^2} e^{-2R_\Gamma/\lambda(k)} \right)$$

$$R_\Gamma = R_{0,\Gamma} + \Delta R_\Gamma \qquad k = \sqrt{2m_e(E - E_0)/\hbar^2}$$

$$\boxed{\chi(k) = \sum_\Gamma \chi(k,\Gamma)}$$

Multiple scattering theory is used to generate the brown terms

$R_{0,\Gamma}$	nominal path length
F_Γ	effective scattering amplitude
Φ_Γ	effective scattering phase shift
λ	mean free path

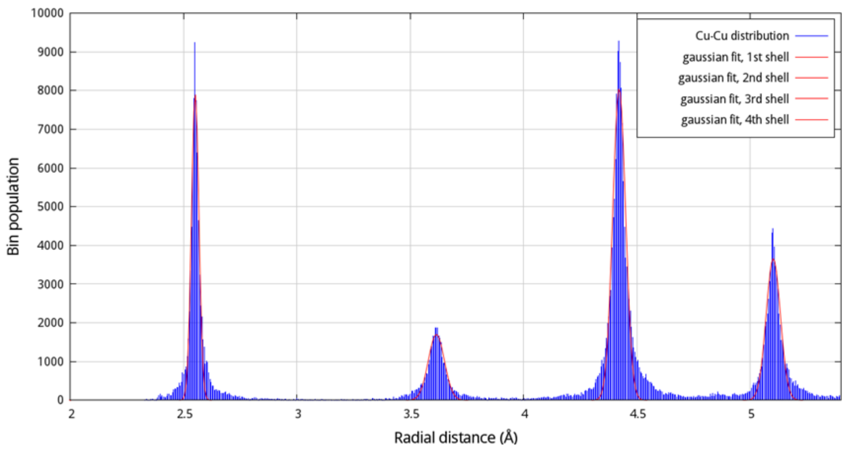
Structural and electronic information is determined from the blue terms

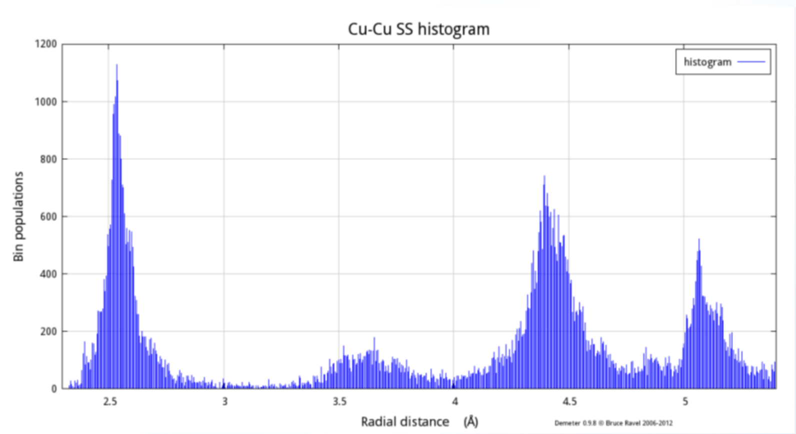
ΔR_Γ	change in half path length
σ_Γ	mean squared displacement
N_Γ	path multiplicity
S_0^2	passive electron reduction
E_0	overall energy shift

Above equation assumes N scattering atoms are at a given distance are distributed with Gaussian disorder contained in the $e^{-2\sigma_\Gamma{}^2 k^2}$ term

Atomic Positions from Molecular Dynamics

The disordered portion of the MD simulation can be emphasized by limiting atoms within 5 Å of the Cu/Nb interface. This presents a PDF that is quite non-Gaussian

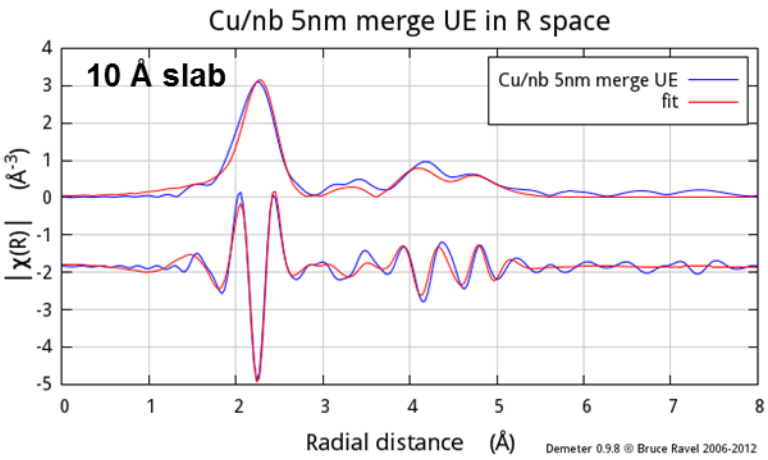


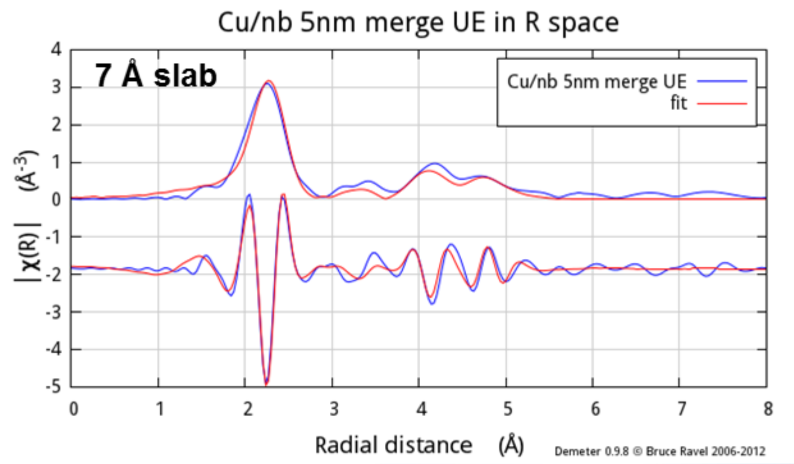


10 Å slab: 340,276 Cu-Cu pairs, binned into 615 bins of size 0.005 Å

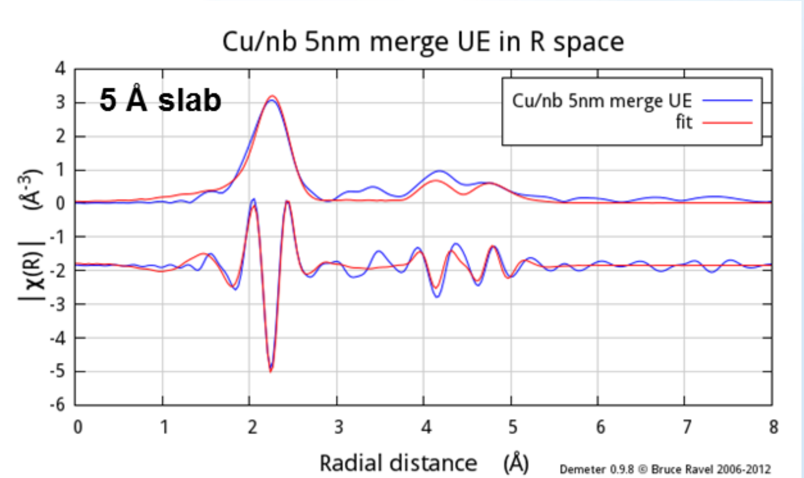
5 Å slab: 87,948 Cu-Cu pairs, binned into 615 bins of size 0.005

Results from the MD/EXAFS models

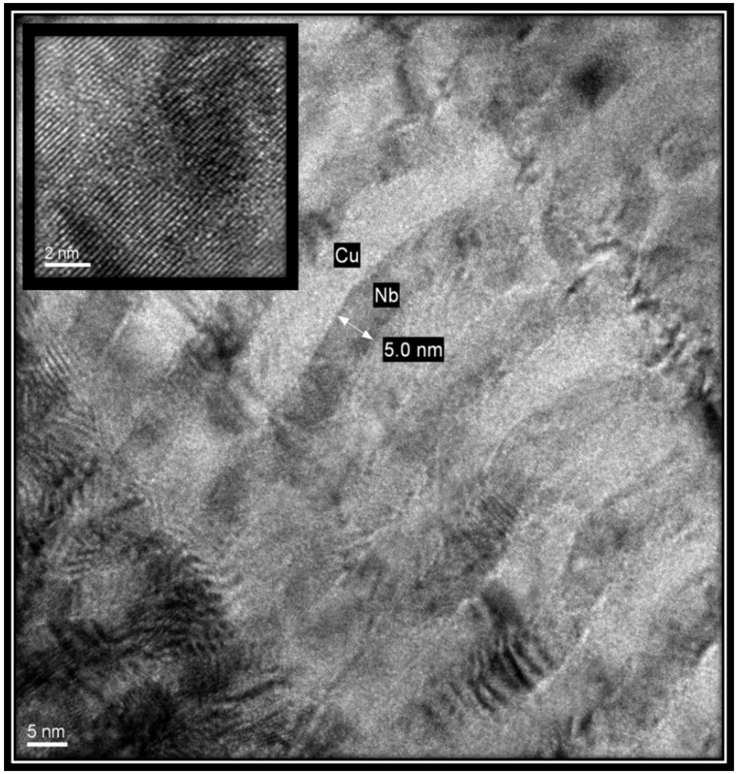


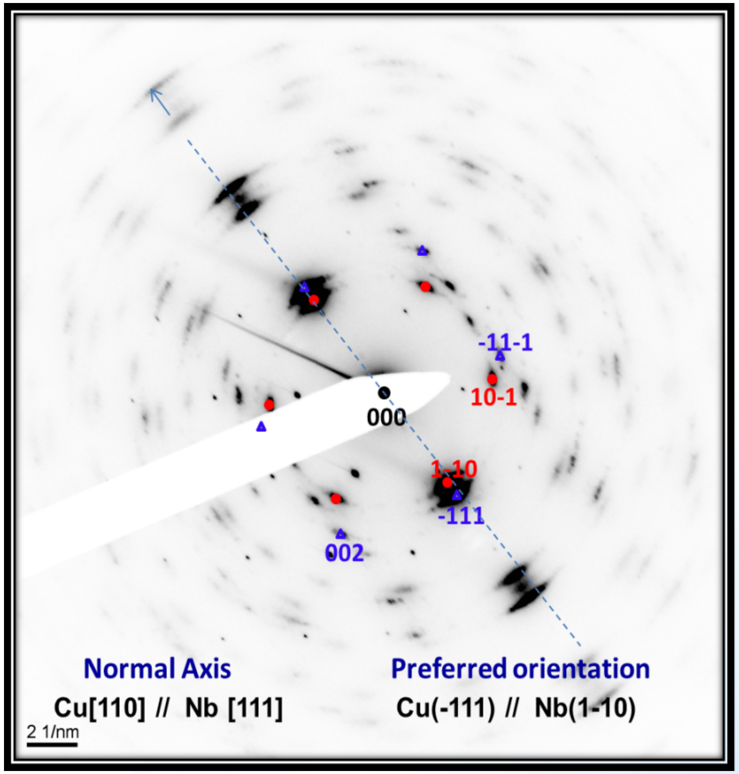


- Increasing contribution from interface (from 10Å to 5Å) results in smaller σ^2 values. However, disorder in the MD simulation is not consistent with the disorder observed in the measured EXAFS data. The "disappearance" of the 2nd shell in the fit with the 5 Å slab suggests this.
- As the samples get thinner, the under-coordination increases. For 20nm, 5nm and 2nm Cu/Nb samples coordination numbers from fit using 7 Å slab are ~ 11.4, 10.4 and 8.5



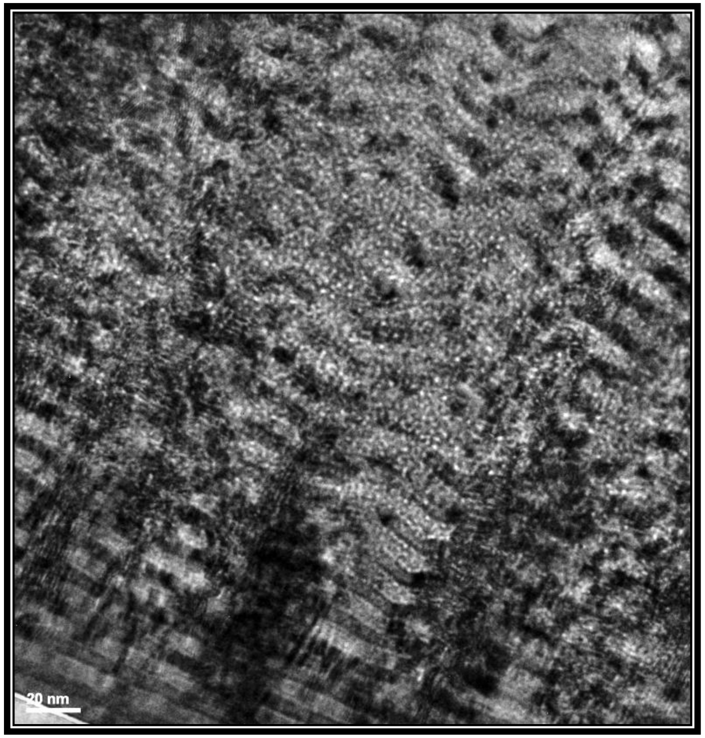
HRTEM results for Cu/Nb nanocomposites

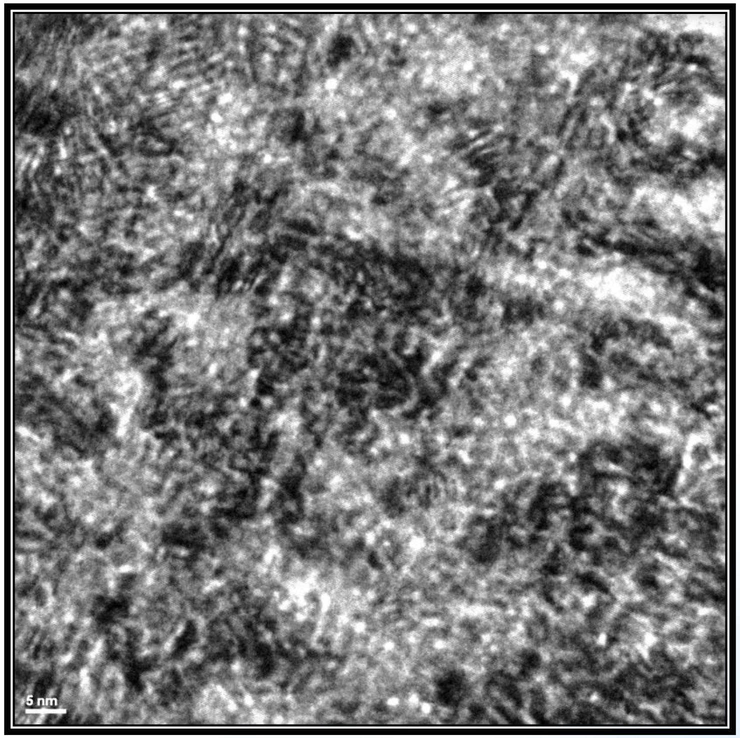




HRTEM of 5nm Cu/Nb nanocomposite control sample: (left and inset): alternating Cu and Nb layers observed with atomic resolution. SAED (right): preferential alignment of Cu (111) and Nb (1-10) in the multilayer normal direction (dashed line) is observed and allows complete indexing of the diffraction pattern.

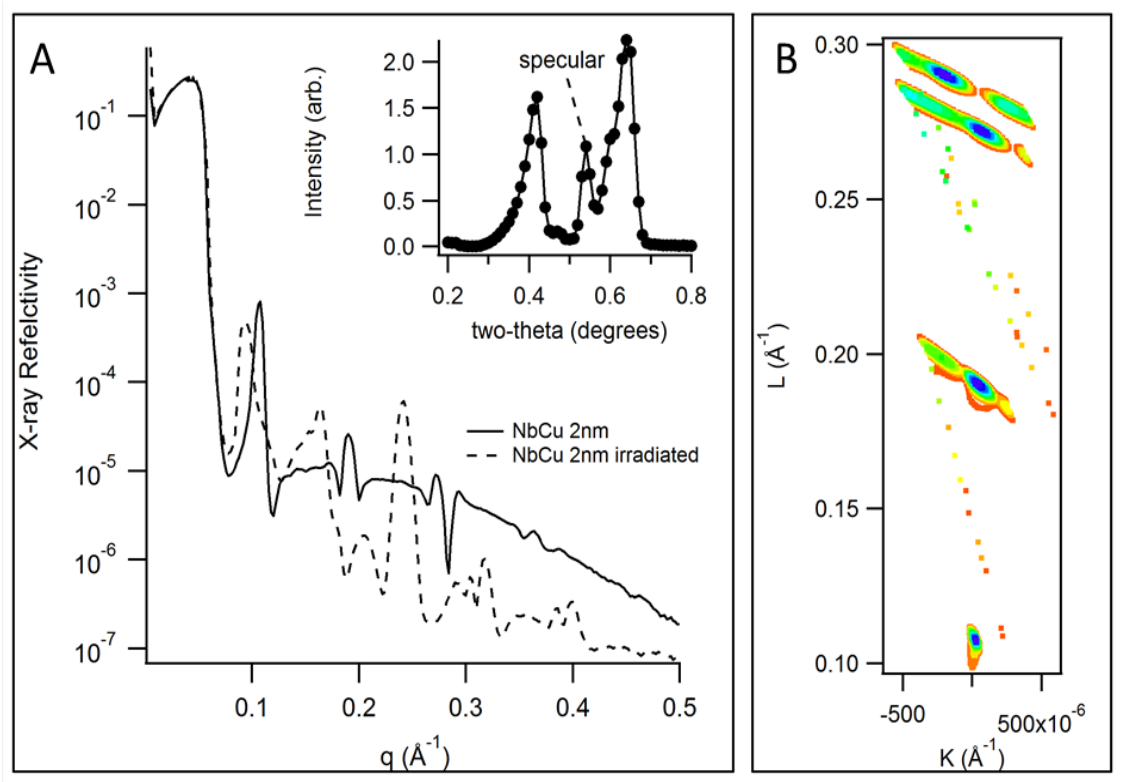
HRTEM results for Cu/Nb nanocomposites





HRTEM of 5nm Cu/Nb nanocomposite sample irradiated with 33KeV He^{+} ions with a dose of 1.5 X10 $^{17}cm^{3}$, (Left): He bubbles observed under defocused condition with peak concentration around 150-180nm under the surface. (Right) He Bubbles observed were very small (~1-2nm).

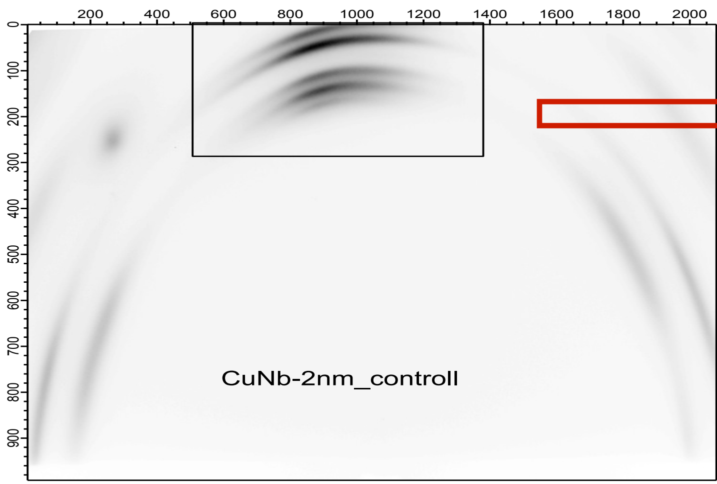
X-Ray Reflectivity Results for Cu/Nb Multilayers

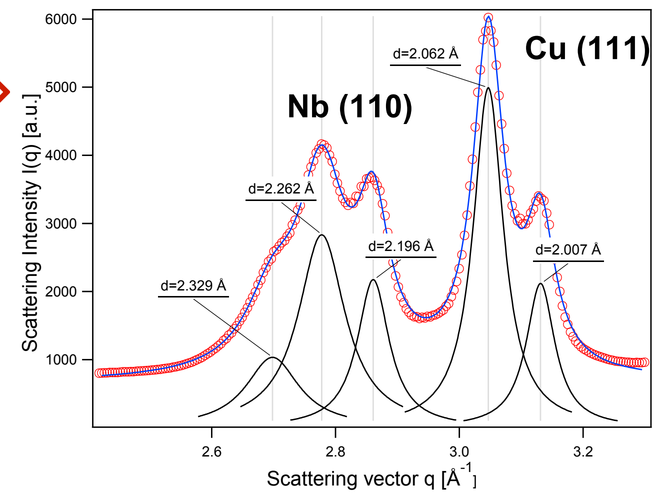


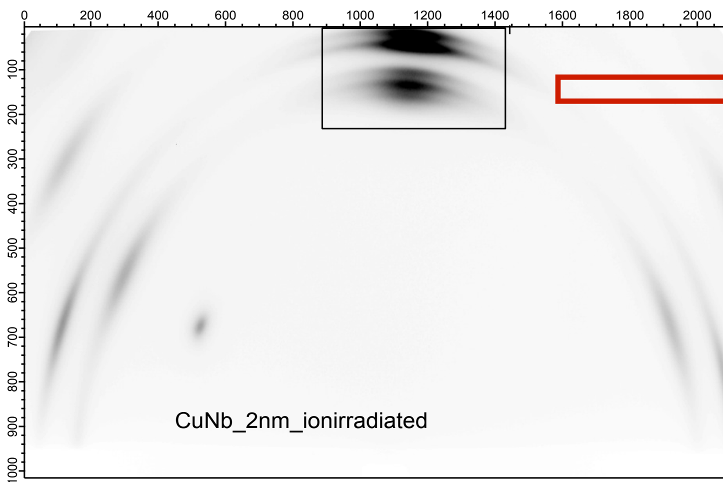
X-Ray Reflectivity data for a 2nm Cu/Nb multilayer samples, showing both as-prepared (Solid-line) and He-irradiated (200KeV) (dashed line) samples

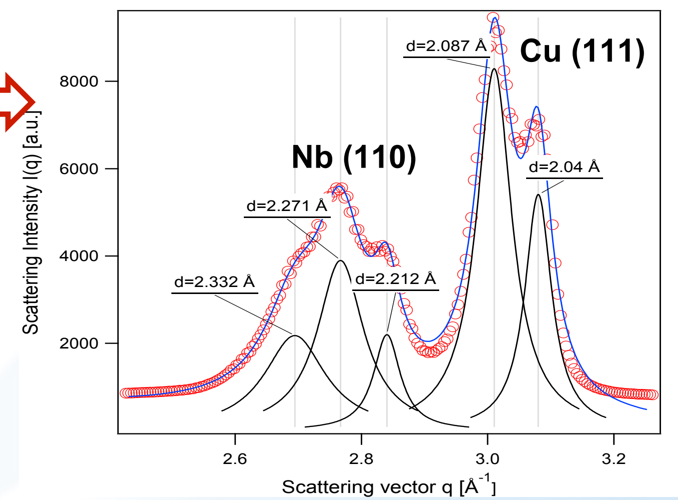
Reflectivity oscillations show that surface roughness of irradiated 2nm Cu/Nb multilayer is significantly greater than the as-prepared multilayer

GI-WAXS Results for Cu/Nb Multilayers









Deformation of the lattices Nb (110) and Cu (111) suggest strain

Structure of nanoparticles in Oxide Dispersion Strengthened Steels

Standards – nanopowders

- Ti
- TiO
- TiO_2
- Y_2TiO_5
- $Y_2Ti_2O_7$
- Y_2O_3

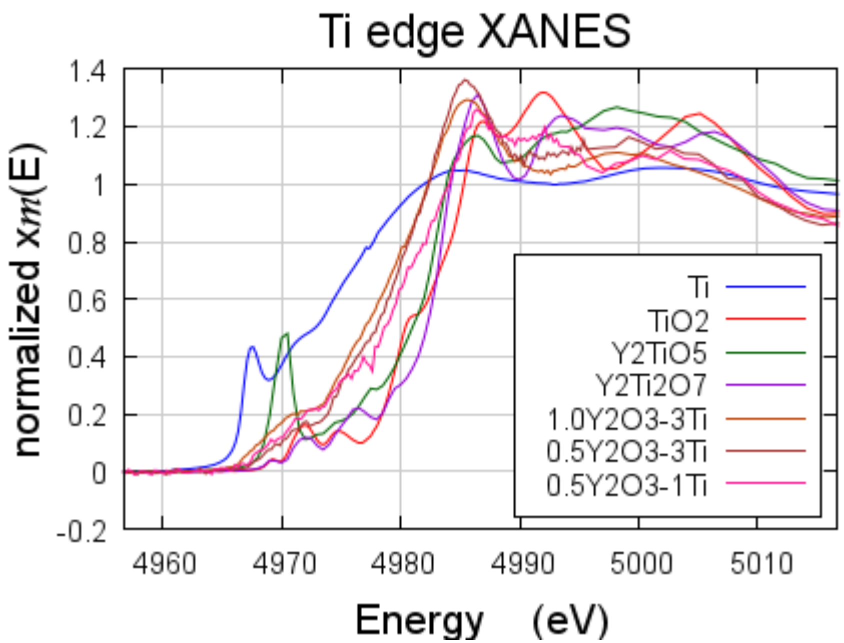
Ti edge

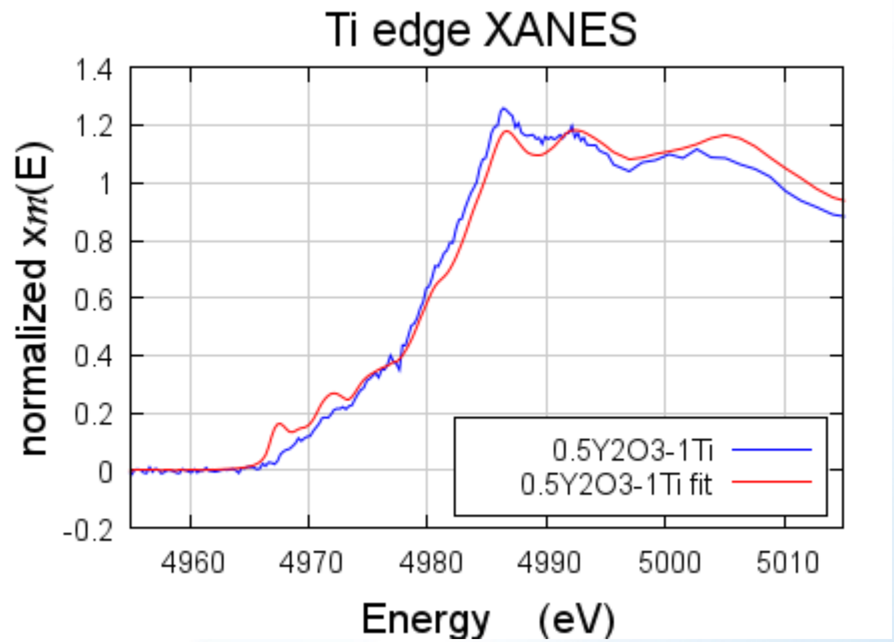
Y edge

Steel powders – ball milled for 10h and annealed at 1150 ^{o}C for 4h

- Fe14Cr3W0.5(Y_2O_3) with Ti/Y=1.57
- Fe14Cr3W0.5(Y_2O_3) with Ti/Y=2.36
- Fe14Cr3W0.5(Y_2O_3) with Ti/Y=3.14
- Fe14Cr3W1.0(Y_2O_3) with Ti/Y=3.1

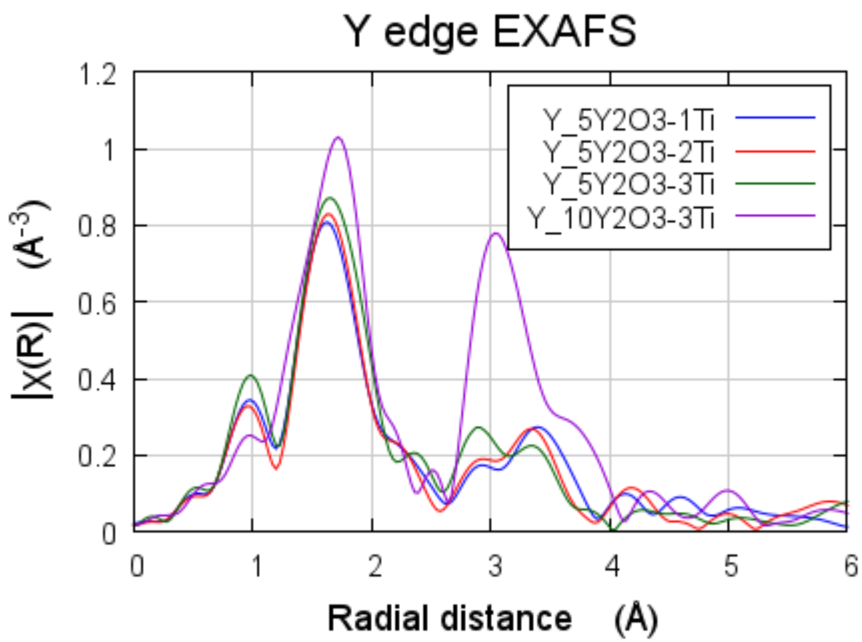
Ti Edge XANES



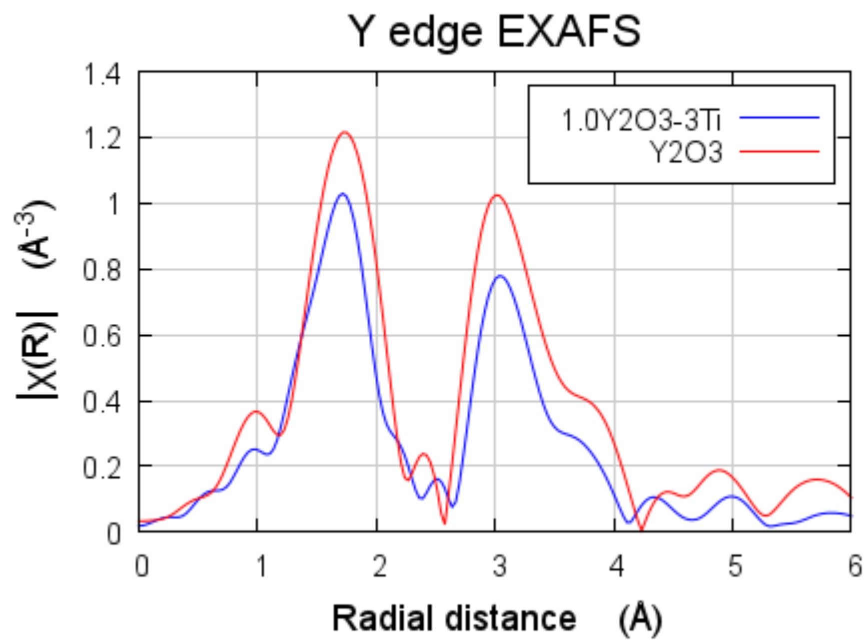


	TiO_2	Ti	$Y_2Ti_2O_7$	Y_2TiO_5
0.5Y2O3-1Ti	40 (8) %	37 (7) %	23 (6) %	0 (0) %

Y Edge EXAFS



Y edge EXAFS
Y_5Y2O3-1Ti
Y_5Y2O3-2Ti
Y_5Y2O3-3Ti
Y_10Y2O3-3Ti
|χ(R)| (Å-3)
Radial distance (Å)



Y edge EXAFS
1.0Y2O3-3Ti
Y2O3
|χ(R)| (Å-3)
Radial distance (Å)

Conclusions

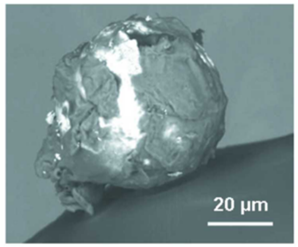
- EXAFS and XANES were collected on Cu/Nb Nanolayers and ODS powder samples
- The disorder in the MD simulation is not consistent with the disorder observed in the measured EXAFS data.
- Several aspects of sample such as curvature of layers introducing strain, defects etc. need to be incorporated in MD simulations.
- EXAFS can contribute to understanding structure of nanofeatures in ODS steels

What Experiment Immediately Comes to Mind??

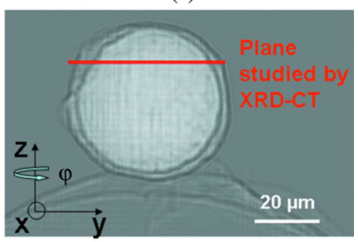
Nuclear Fuel

Images from Dr. H. Palancher, CEA

UMo spherical particles isolated on top of a capillary by (*c*) SEM and (*d*) X-ray magnified radiograph.

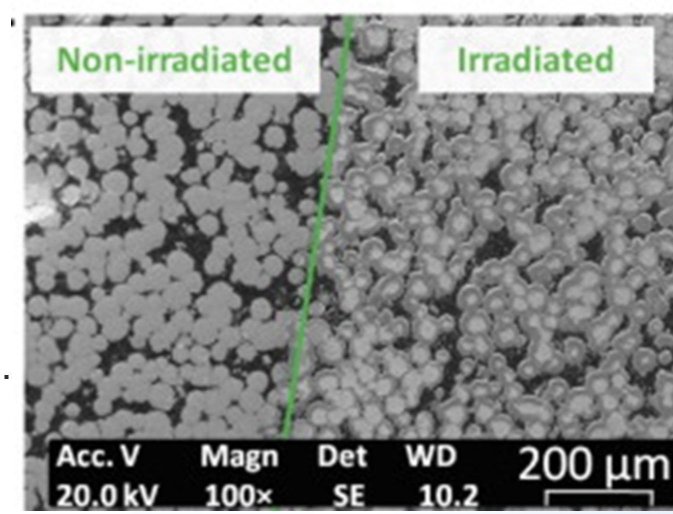


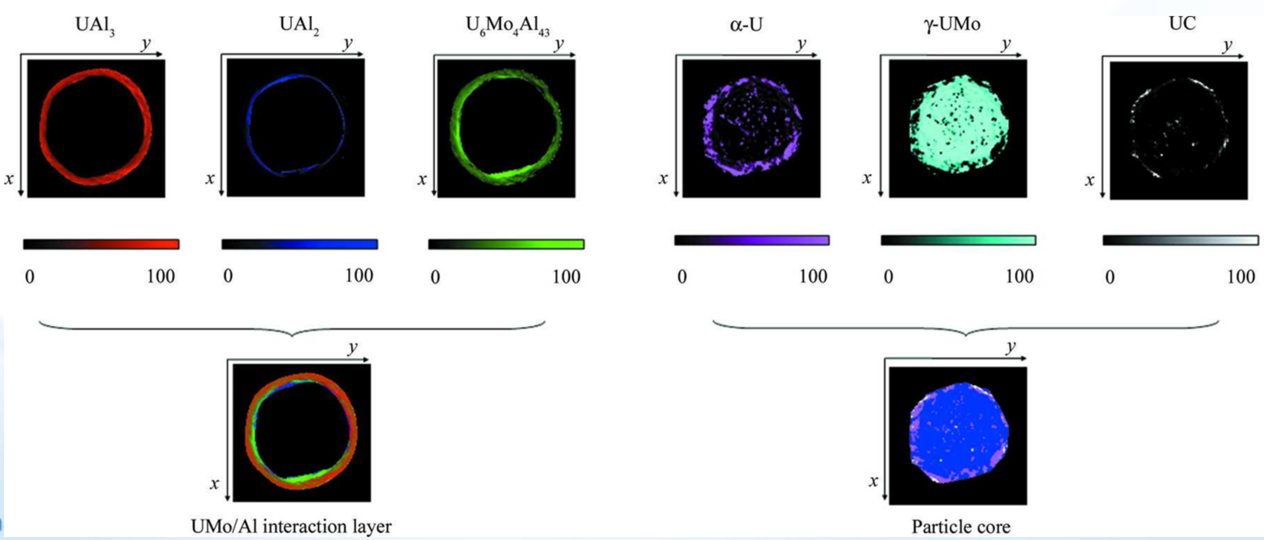
(*c*)



(*d*)

Optical micrograph of irradiated and un-irradiated area at the UMo10/Al sample surface.





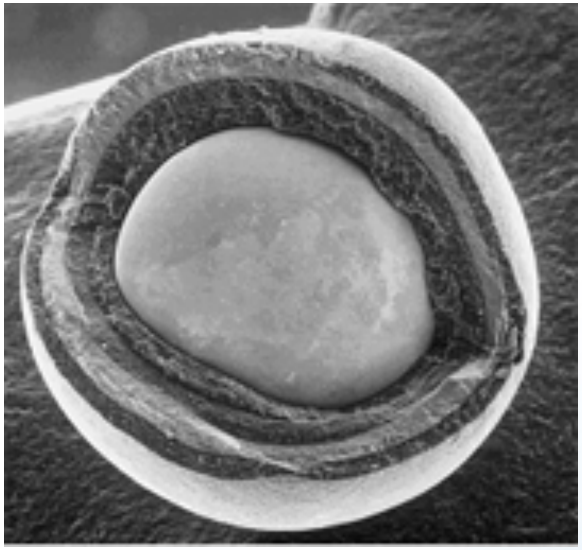
Reconstructed weight fraction W^R_i (x, y) slices.

Proposed Experiment: TRISO Particle

- Primary containment in Graphite Reactors
- Very High Temperature (~1600 C in accident conditions)
- Fission products diffuse through clad; breach containment

Experiment (collaboration with ORNL)

- Map the diffusion Silver and Palladium in coatings
- Chemical states
- 10 nanometer resolution
- Etch out the spent fuel, so sample is not radioactive



500 micron sphere (OD)
UO_2 or (UC or UCO) kernel
Four coating layers

- Porous C buffer
- PyC
- SiC
- PyC

In-situ studies of corrosion in zirconium alloys for nuclear energy systems

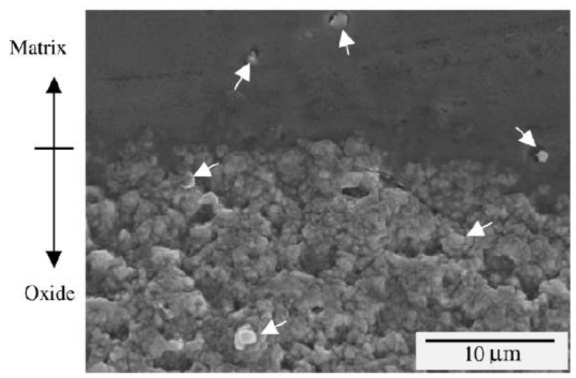
Simerjeet K Gill, Nuclear Sciences and Technology

Problem Statement: Understanding the corrosion in zirconium alloys by in-situ diffraction studies at NSLS II.

Importance:

Rapid reaction of zirconium alloys with steam at high temperatures under Loss of Coolant Accidents (LOCA) conditions leads to corrosion and break away oxidation resulting in hydrogen gas production and failure of cladding in reactors. Understanding corrosion and engineering alloys with protective oxides that can withstand longer exposures in the reactor are crucial for safer nuclear power. Corrosion of Zirconium alloys important is an issue for achieving higher burnup in today reactors.

Approach:



- Materials: Zirconium alloys (Zircaloy-4, ZIRLO, Zr-Nb alloys).
- Experiments
  - Study of oxide microstructures formed to explain differences in corrosion rates of different Zr alloys.
  - To determine the morphology of the oxide layers (grain size and shape, strains in the grains, texture, cracks, oxide phases formed and their orientation, incorporation of precipitates, relationship between orientation of oxide grains and matrix grains).
  - Parameters to be varied: Alloy chemistry and microstructure (grain size and texture), the corrosion environment including temperature and exposure time.

Experiment at NSLS-II

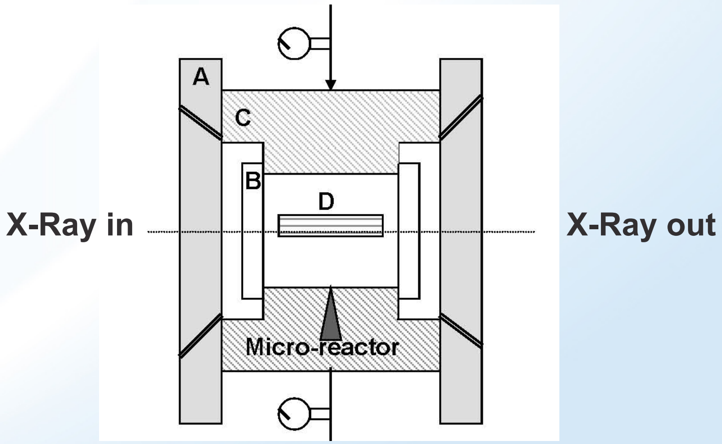
Technique:
- In situ characterization of cladding materials and corrosion films using diffraction and high Temperature cell (T=400C-600 ºC).
- X-ray microdiffraction

Impact:
- Gain insight of underlying mechanisms and oxide microstructures formed during corrosion of nuclear alloys.
- Elucidate the detailed microstructure of oxide layer.
- Engineer new corrosion resistant alloys and design better cladding materials for LOCA conditions.

Technology Development: Structural materials for fission/fusion reactors, new materials for GEN IV reactors more resistant to LOCA conditions, life-extension of aging materials in current reactors.

Collaboration: Dr Arthur Motta from Penn State University

What does the sample environment look like?
What are the demands on the environment?



Micro-reactor for in-situ studies

Additional Questions

Which elements are of most interest?

- Cu and Nb
- Ti and Y
- Ag and Pd
- Fe, Zr, Cr, Ni, U

High Resolution versus Large Sample Area?

- High Resolution!
- And Both!
- Zooming-in is always nice

Which techniques are crucial?

- Imaging with elemental mapping
- Microdiffraction

Extra Slides

X-ray Absorption Spectroscopy

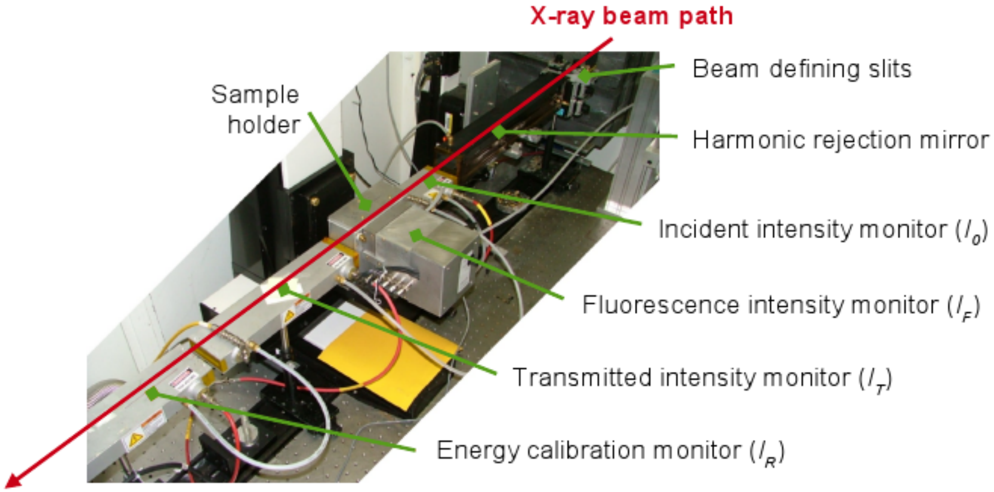
X-ray Absorption Near-edge Spectroscopy (XANES)

- Formal oxidation state
- Coordination chemistry
- Fitting with linear combinations of standards

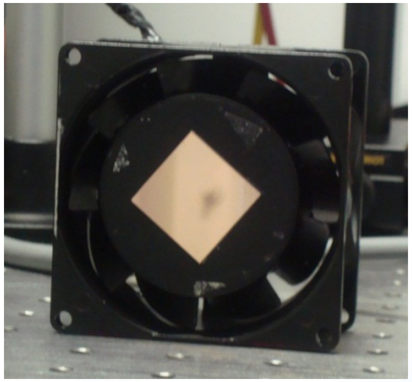
Extended X-ray Absorption Fine Structure (EXAFS)

- Distances
- Coordination number
- Species of surrounding atoms
- Fitting to theoretical model from atomic positions
- Fitting to theoretical model with atomic positions from Molecular Dynamics

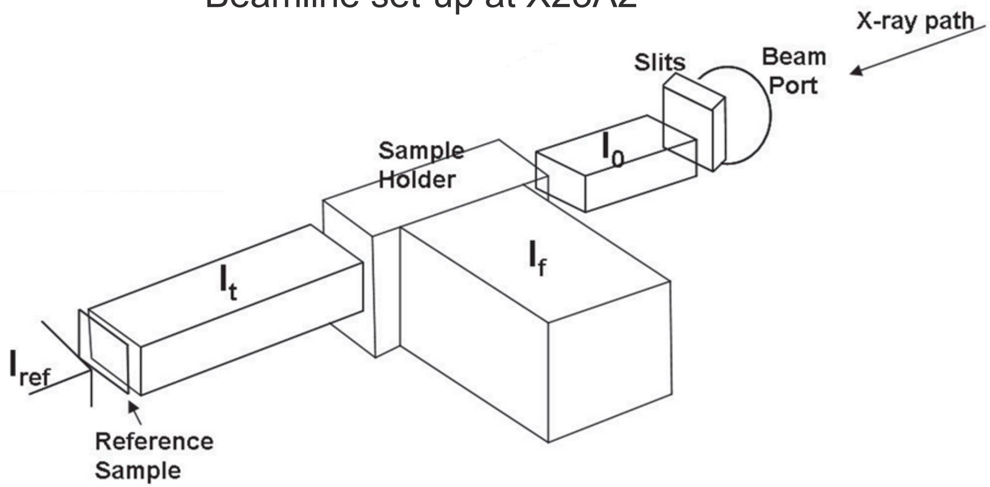
Extended X-Ray Absorption Fine Structure (EXAFS) studies for Cu/Nb Multilayers



Beamline set-up at X23A2



Spinning sample stage



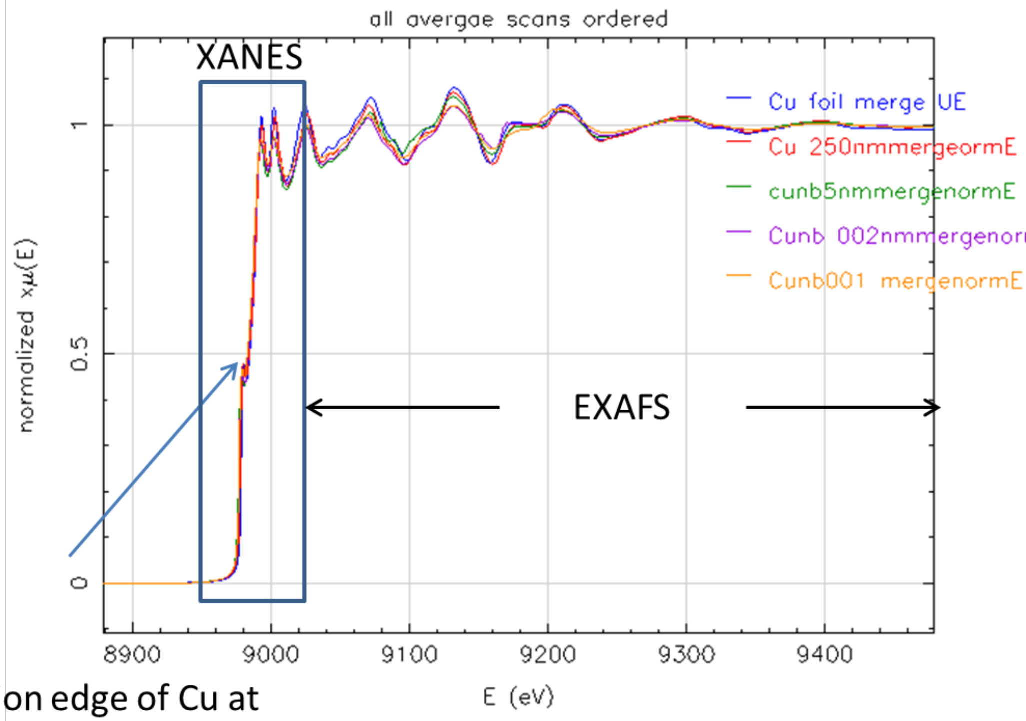
Schematic showing beamline set-up for EXAFS florescence measurements

EXAFS in flourescence mode

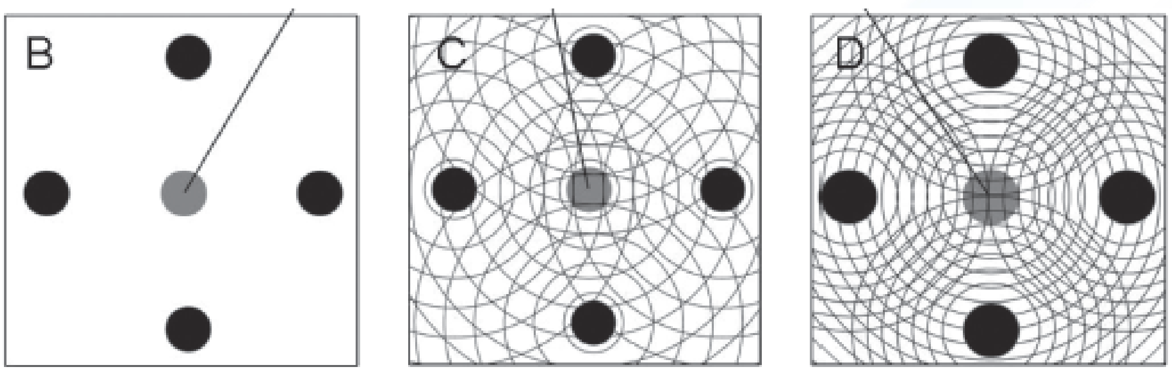
$\mu x \propto I_f/I_0$

μ is absorption coefficient
x is sample thickness
I_f is fluorescence X-rays
I_0 is incident X-rays

EXAFS Data from Cu/Nb Multilayer Composites



Absorption edge of Cu at



- X-Ray Absorption Near Edge Structure (XANES) -50 to +200eV relative to the edge energy
- Extended X-Ray absorption Fine Structure (EXAFS) normalized oscillatory part of the absorption coefficient above the absorption edge to ~ 1000 eV or higher